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THERMODYNAMIC CHARTS FOR THE COMBUSTION PROCESS IN DIESEL CYCLES

F. E. SWIDERSKI

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U. S. Naval Postgraduate School
Monterey, California

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THERMODYNAMIC CHARTS
FOR THE COMBUSTION PROCESS
IN DIESEL CYCLES

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F. E. Swiderski

PREFACE

Though a number of thermodynamic charts for internal combustion processes have been prepared in the past two decades, the project by Lt. William F. Farrell, Jr., USN, "Thermodynamic Chart for The Combustion Process in Diesel Cycles", was one of the first to cover the pressure, temperature and a typical fuel-air ratio of diesel cycles.

This project presents thermodynamic charts of two diesel fuel-air ratios, being assumed maximum and minimum ratios that would be used in diesel cycles, covering the temperatures and pressures used by Lt. Farrell in his project. Thus this is a continuation of the project started by him. The ratios used will enable the user to extrapolate or interpolate between the values used by the author and those of Lt. Farrell.

Of a necessity, much of the written material is a repetition of the work done by Lt. Farrell. Much of Lt. Farrell's work and methods have been checked.

The analysis and computations necessary for this project and the construction of the thermodynamic charts was made during the period February, 1952 through June, 1952, by the author.

THERMODYNAMIC CHARTS FOR THE COMBUSTION PROCESS IN DIESEL CYCLES

by

Francis E. Swiderski
Commander, United States Navy

Submitted in partial fulfillment
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for
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Ia Thermodynamic Charts for Combustion Process in Diesel Cycles Rear Cover

LIST OF SYMBOLS

P	Pressure (total), in atmospheres
P_i	Pressure (partial), in atmospheres
p	Pressure (total), lbs./sq. in.
T	Temperature, °Rankine
V	Volume, cubic feet
E	Internal Energy, B.T.U., above CO_2, H_2O (vapor), O_2 and air-N_2 at 100°F.
E_s	Sensible Internal Energy, $(E-Q_v)$, in B.T.U.
Q_v	Internal Energy of Combustion, at 100°F., of unburned fuel in equilibrium mixture at temperature T, in B.T.U.
H	Enthalpy, B.T.U., $E = J(pV)$
S	Entropy, B.T.U./°Rankine, above CO_2, H_2O (vapor), O_2 and air-N_2, each at one atmosphere and 100°F
R	Universal gas constant
J	Conversion factor, 1 B.T.U. 778 ft. lbs.
K	Mean Specific Heat Ratio
K_1-K_6	Equilibrium constants
x_i	Mole fraction of each chemical species at equilibrium
m	Moles of each chemical species at equilibrium
Σm	Total moles of combustion products

CHAPTER I

INTRODUCTION

The large fraction of combustion processes of interest to the engineer involves burning of a hydrocarbon of fairly moderate volatility in air. For purposes of analysis by thermodynamic chart, an internal combustion engine cycle may be divided into (A) low temperature regions where chemical dissociation does not occur, or negligible in importance, and (B) high temperature regions, reached in the combustion of the fuel, where chemical dissociation may become of appreciable magnitude.

Charts prepared by H. C. Hottel, G. C. Williams and C. N. Satterfield in 1949 (2), cover both the above regions for the gasoline engine cycle, and are satisfactory for use with diesel engine cycles in region (A). They do not, however, cover the temperature range and pressure range of the diesel during combustion, i.e., in region (B).

The thermodynamic charts presented in this project cover the pressure and temperature range of the combustion portion of the diesel cycle for two limiting diesel fuel-air ratios. They have been constructed on the same material and temperature bases as charts for gasoline engines in region (B), and thus may be used in conjunction with charts representing the unburned mixture, as prepared by Hottel, Williams and Satterfield (2). Values of equilibrium constants and thermodynamic property values used here are consistent with those used by Hottel, Williams and Satterfield (2).

CHAPTER II

BASIC CONSIDERATIONS AND DATA

1. Data Used

It was suggested by Professor D. Kavanaugh, of the Engineering School, of the United States Naval Postgraduate School, that the charts to be constructed have fuel-air ratios below and above the fuel-air ratios used by Lt. Farrell. The following data was used:

Fuel-Air Ratio: 0.77 (130% theoretical air).

0.40 (250% theoretical air).

Pressure Range: 800 p.s.i. to 1500 p.s.i.

Temperature Range: 3000° Rankine to 4500° Rankine.

2. Chemical Dissociation

At the high temperatures reached in the combustion process of the diesel engine there may be many different molecular species present in varying amounts, due to chemical dissociation of the working fluid. The requirement of chemical equilibrium necessitates consideration of the effect of the species on the thermodynamic properties of the burned mixture. There are ten molecular species (N_2, O_2, CO_2, H_2O, NO, OH, CO, O, H_2, and H) present in sufficient quantity to require consideration in this development. In the course of this project, it was found that the effects of the minor species (NO, OH, CO, O, H_2, H) were of definite importance in the temperature and pressure range used. In Figure 1. is shown the effect of temperature on the relative magnitude of these species for one representative pressure for both fuel-air ratios. It is apparent that the magnitudes of these minor species become appreciable

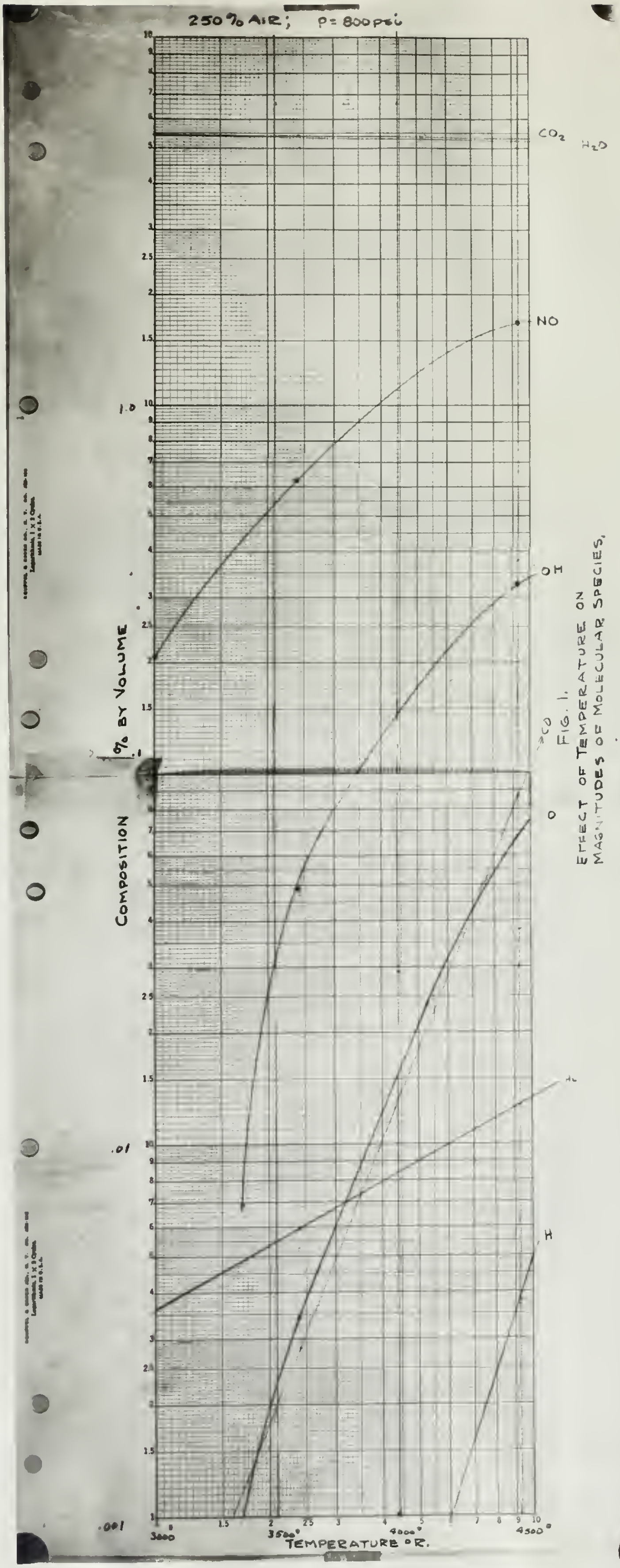

FIG. 1.
EFFECT OF TEMPERATURE ON MAGNITUDES OF MOLECULAR SPECIES.

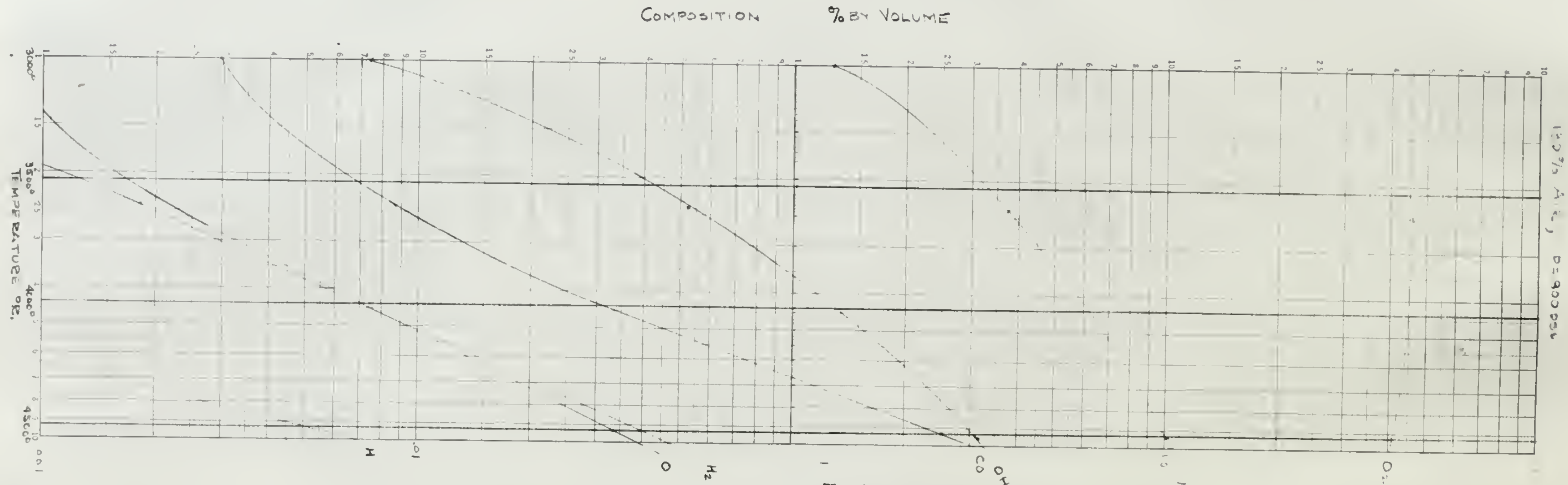

Fig. 1a
EFFECT OF TEMPERATURE ON
MAGNITUDES OF [illegible]

at the higher temperatures, and cannot be neglected in computations, without resulting error. Particularly is this true of the species NO and OH, which frequently are neglected in determinations of burned mixture composition.

3. Ideal Gas Law

Computations involving composition of the burned mixture together with critical pressures and temperatures of the component species indicate that the burned mixtures behave as if their critical pressures and temperatures are approximately 30 atmospheres and 350° Rankine, respectively. At the elevated temperatures of the chart deviations from the ideal gas law are insignificant. Therefore, the chart is based on the equation of state for ideal gases.

4. Fundamental Data

The fundamental data required for calculation of these charts are: (a) equilibrium constants as functions of temperature, and (b) various heats of reaction. The author has accepted for his calculations the same data on internal energies, enthalpies, entropies, and equilibrium constants as did Hottel, Williams and Satterfield (2), and the computations of Lt. Farrell based on the above. The method of determining the changes in the thermodynamic properties for the chemical reaction in question is given in Appendix I, page 21; the method of obtaining the actual equilibrium constants used in the calculation of composition of combustion products in equilibrium at the various temperatures and pressures is described briefly in Appendix I, page 19.

Composition of air: On a basis of 100 moles of dry air, a composition of 20.99 moles of oxygen and 79.01 moles of nitrogen was used. In at the higher temperatures, and cannot be neglected in computations, without resulting error. Particularly is this true of the species NO and O_2, which frequently are neglected in determinations of normal mixture compositions.

5. Ideal Gas Law

Computations involving composition of the normal mixture together with critical pressures and temperatures of the component species indicate that the normal mixture behaves as if such critical pressure and temperature are approximately 30 atmospheres and 280° Kelvin, respectively. At the elevated temperatures of the chart deviations from the ideal gas law are insignificant. Therefore, the chart is based on the equation of state for ideal gases.

6. Fundamental Data

The fundamental data required for calculation of these charts are: (a) equilibrium constants as functions of temperature, and (b) enthalpy heats of reaction. The author has accepted for his calculations the same data on internal energies, enthalpies, entropies, and equilibrium constants as did Hershey, Williams and Satterfield (21), and the computations of Dr. Farrell based on his charts. The method of determining the changes in the thermodynamic properties for the chemical reaction in question is given in Appendix I, page 21; the method of obtaining the actual equilibrium constants used in the calculation of composition of combustion products in equilibrium at the various temperatures and pressures is described briefly in Appendix I, page 19.

Composition of air. On a basis of 100 moles of dry air, a composition of 20.99 moles of oxygen and 79.01 moles of nitrogen was used. In actuality, the nitrogen above has minor components of argon, carbon dioxide, and hydrogen included, and might better be called Air-Nitrogen. The above composition was used in calculating thermodynamic properties; but pure nitrogen was used in equilibrium calculations, which made but a negligible change in the amount of NO present.

Composition of fuel: The fuel chosen was the hydrocarbon $(CH_2)_x$, which has a hydrogen-carbon ratio considered adequately representative of diesel fuel.

Other constants:

1. Gas Constant R = 1.987 cal./°K, gram-mole.
2. Apparent Formula Mass of Air = 28.95 (which agrees with the above air composition.)
3. Atomic masses from 1936 International Tables.
4. Conversion Factor: 1 atmosphere = 14.696 p.s.i.
5. Conversion Factor: 1 cal./gram-mole = 1.80 BTU/lb.-mole.
6. Conversion Factor: 1 lb.-mole burned mixture = 0.0024135 lb. of air.

CHAPTER III

PROCEDURE

1. Analysis

If definitely fixed quantities of carbon, hydrogen, oxygen and nitrogen are permitted to come into equilibrium, two of the properties of the resultant mixture may be fixed, and will be sufficient to completely define the composition of the mixture, and hence its thermodynamic properties. Pressure and temperature were the properties selected in this work.

It was considered that the chemical dissociation would produce combustion products containing the following molecular species: N_2, O_2, CO_2, H_2O, CO, H_2, H, OH, O and NO. The relative magnitudes of these species, at the fixed fuel-air ratio, depend on the pressure and temperature. The method used to calculate these magnitudes at a sample pressure and temperature, using determined data on equilibrium constants, is shown in Appendix II.

2. Material Basis

The material basis of the chart is the quantity of material which contains nitrogen and oxygen equivalent to one pound of air.

For complete combustion:

$$(CH_2)_x + x(1.5\,O_2 + 3.76\,\boxed{1.5}\,N_2) = x(CO_2 + H_2O + 5.64\,N_2)$$

For a fuel-air ratio of 0.77, there are 1.95 moles of oxygen and 7.332 moles of nitrogen, or 9.282 moles of air, for each CH_2 unit of fuel. The mass of air is (9.282) (28.95) = 268.714 pounds; the mass of fuel (1)(12) + (2)(1.008) = 14.016 pounds. The mass of fuel associated with one pound of air is then 0.05216 pounds. For a fuel-air ratio of 0.40, there are 3.75 moles of oxygen and 14.1 moles of nitrogen, or 17.85 moles of air, for

each CH_2 unit of fuel. The mass of air is 14.016 pounds. The mass of fuel associated with one pound of air is then .027123 pounds. The mass basis is necessary for consistency because the number of moles of combustion products varies at elevated temperatures with variation of any thermodynamic property.

3. Determination of Thermodynamic Properties

The temperature base for the chart was selected as 100°F. The values of internal energy and entropy, obtained from Table 6, Appendix A, Hottel, Williams, and Satterfield, (2) were converted to this temperature base as described and illustrated in Appendix I. To determine the internal energy of the combustion products at each selected temperature and pressure, the procedure is to multiply the mole fraction of each molecular species in the products, by its corresponding value of internal energy, corrected to proper temperature base, sum up these products for all ten species, and convert to the proper material basis for the chart; thus

$$E_{mix} = \sum \chi_i E_i$$

Entropy involves not only an additive factor similar to that shown above for internal energy, but also the entropy of mixing; that is, the entropy of the mixture is

$$S_{mix} = \sum (\chi_i S_i - \chi_i R \ln P_i)$$

where χ_i is the mole fraction of each species, S_i is the molar entropy of each species at one atmosphere pressure and each temperature, corrected to the proper temperature base, R is the gas constant, and P_i is the partial pressure of the components, in atmospheres, and also equals $\chi_i P$, where P is the total pressure of the mixture in atmospheres. The entropy S_{mix} is corrected to the proper material base for

the chart. The enthalpy of the mixture is obtained from the thermodynamic relation

$$H_{mix} = E_{mix} + p\,V/J = E_{mix} + RT$$

The volume at each pressure and temperature is obtained from the ideal gas law:

$$V_{mix} = (\Sigma m)R'T/144p$$

where (Σm) is the total moles of the mixture at each temperature and pressure, R' is the gas constant (1545 BTU/°R. lb-mole) and p is the total pressure in pounds per square inch. This volume is then converted to the proper material basis of the chart.

4. Description of Chart

The thermodynamic properties represented on the chart are as follows:

(a) Temperature - T, degrees Rankine. Nearly horizontal solid lines at 200 degrees intervals.

(b) Pressure - p, pounds per square inch. Diagonal solid lines at 100 p.s.i. intervals.

(c) Volume - V, cubic feet per pound of original air. Diagonal dashed lines with greater slope than the pressure lines, at 0.1 or 0.2 cubic foot intervals.

(d) Internal Energy - E, BTU per pound of original air. Ordinate of chart.

(e) Entropy - S, BTU/°Rankine per pound of original air. Abscissa of chart.

(f) Enthalpy - H, BTU per pound of original air. Nearly horizontal dashed lines, superimposed on the chart to eliminate the necessity of using the relation $H = E + RT$.

5. Method of Reading the Chart

To illustrate reading the chart let it be desired to determine the thermodynamic properties of the products of combustion of one pound of air with (CH_2) x vapor at T 3600° Rankine and p 1200 p.s.i. The original mixture contains 150% excess air. Locate the intersection of the lined corresponding to the above temperature and pressure, and read directly that the volume is 1.8 cubic feet; the internal energy is 682.1 BTU; the enthalpy is 947.2 BTU; and the entropy is 0.269 BTU/° Rankine. Interpolation between temperature and enthalpy lines is substantially linear. In actual cycle analysis employing the chart, the known thermodynamic properties will be more probably pressure and either internal energy or enthalpy, but the procedure in reading the chart remains the same.

6. Use of the Chart.

The chart is designed for use in conjunction with diagrams representative of the unburned mixture existing prior to combustion, in analyzing diesel cycles. Such diagrams have been prepared byHottel, Williams, and Satterfield, (2). The author'scharts indicate the thermodynamic properties of the burned mixture as a result of the combustion process.

CHAPTER IV

A DISCUSSION OF THE SYSTEM BELOW 3000° RANKINE

1. Basic Requirements.

To permit determination of the thermodynamic properties of the burned mixture as a result of isentropic expansion to a point where the exhaust valve opens, a low pressure-low temperature chart, of substantially the same entropy limits as the author's chart, is required. The approximate temperature and pressure ranges for this chart are 900° Rankine to 2900° Rankine, and 14.7 p.s.i. to 190 p.s.i. respectively.

2. Frozen Equilibria.

Chemical equilibrium has been assumed to exist at all temperatures above 3000° Rankine, where the chemical reaction velocity is quite high. However, when the gas mixture is rapidly cooled below 3000° Rankine, the composition is found to correspond to that at some higher temperature, at which the composition "froze". Considering that in diesel cycles an isentropic path is closest to the actual path to the system below 3000° Rankine, the pressure effect on composition was taken into account by the assumption that the composition of a mixture below 3000° Rankine, was that of the mixture at 3000° Rankine, at the same entropy. Experimental validation of this assumption is quoted in Chapter V, Robinson (5), and is consistent, in this temperature and pressure range, with the value of 2880° Rankine, used by Hottel, Williams, and Satterfield (2).

3. Determination of Thermodynamic Properties.

The composition of the burned mixture at 3000° Rankine and at various pressures is determined as shown in Appendix II. The entropy

of the mixture at 3000° Rankine and the above pressure is determined as described in paragraph 3 of Chapter III. As stated in paragraph 1 above, the composition of the burned mixture at any temperature below 3000° Rankine is that of the mixture at 3000° Rankine at the same entropy. Thus, selection of any temperature T in this region fixes two thermodynamic properties - temperature and entropy - and these are sufficient to define the remaining thermodynamic properties of the mixture. The internal energy and enthalpy at each temperature T is then obtained in the manner described in paragraph 3, Chapter III, using the mixture composition at 3000° Rankine at each entropy. To obtain pressure (p) and volume (V), the equations for the isentropic process by which this region is entered in the cycle, from the region above 3000° Rankine, are used. These are, at any temperature T and entropy S:

$$p = p' \left(\frac{T}{T_1}\right)^{k/k-1} \qquad \text{and} \qquad V = V_1 \left(\frac{T_1}{T}\right)^{1/k-1}$$

where p_1 and V_1 are the pressure and volume at $T_1 = 3000°$ Rankine, and k is the mean specific heat ratio between the temperature T and T_1. Values of the specific heat ratio for the $(CH_2)_x$ fuel with 130% and 250% air, at any temperature between 300° Rankine and 4000° Rankine, may be obtained from tables in the Gas Tables (3), by interpolation and extrapolation. The method of obtaining the mean specific heat ratio between any two temperatures, when the specific heat ratios at these limiting temperatures are known, is set forth in Kiefer, Stuart and Kinney (4).

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APPENDIX I

TABLE I

Equilibrium Constants For Chemical Reactions

T°R.	K_1	K_2	K_3	K_4	K_5	K_6
3000	3.406	$9.1658\text{x}10^{-8}$	$1.816\text{x}10^{-10}$	$3.981\text{x}10^{-10}$	$1.014\text{x}10^{-4}$	$5.053\text{x}10^{-6}$
3600	4.782	$5.777\text{x}10^{-7}$	$7.925\text{x}10^{-8}$	$2.037\text{x}10^{-7}$	$1.597\text{x}10^{-3}$	$1.627\text{x}10^{-4}$
4500	6.435	$3.512\text{x}10^{-4}$	$3.451\text{x}10^{-5}$	$9.122\text{x}10^{-5}$	$2.514\text{x}10^{-2}$	$5.232\text{x}10^{-3}$

$$K_1 = \frac{P_{CO} P_{H_2O}}{P_{CO_2} P_{H_2}} \qquad K_4 = \frac{P_O P_{H_2}}{P_{H_2O}}$$

$$K_2 = \frac{P_{NO} P_{H_2}}{P_{H_2O} P_{N_2}^{1/2}} \qquad K_5 = \frac{P_H}{P_{H_2}^{1/2}}$$

$$K_3 = \frac{P_{O_2} P_{H_2}^2}{P^2_{H_2O}} \qquad K_6 = \frac{P_{OH} P_{H_2}^{1/2}}{P_{H_2O}}$$

P_i in above is partial pressure in atmospheres, of each molecular species.

Equilibrium constants listed above were calculated from the series of values listed in Table 7, Appendix A, of Hottel, Williams, and Satterfield (2) by interpolation, employing the linear relationship between the reciprocal of absolute temperature $(1/°K.)$ and the natural logarithmic value of the equilibrium constant $(\log_e K_n)$.

TABLE II

Thermodynamic Properties of Molecular Species

	Internal Energy			Enthalpy		
	E			H		
Species	3000°	3600°	4500°	3000°	3600°	4500°
CO_2	14326	18448	24898	17638	22422	29866
H_2o	10659	13979	19301	13971	17953	24269
Air–N_2	7765	9992	13266	11077	13966	18234
O_2	8396	10712	14301	11709	14686	19269
CO	75265	77467	80846	78577	81441	85814
H_2	64718	66733	69925	68030	70707	74895
H	84601	85594	87085	87915	89568	92053
OH	45423	47473	50721	48735	51447	55689
NO	29696	31928	35349	33008	35902	40317
O	62799	63792	65283	66111	67766	70251

The units of the above are calories /g-mole.

The values shown above were obtained from those in Table 6, Appendix A, Hottel, Williams, and Satterfield (2), in the following manner, using the internal energy of species at as an example.

The internal energy of any species at temperature T equals $E_S + Q_V$ where E_S is the heat released by cooling the gas at constant volume to the temperature base of the chart ($100^\circ F = 311^\circ K$), and Q_V is the heat of combustion of the gas at constant volume at $100^\circ F$. E_S is the value of E of the species at temperature T minus the value of E of the species at $100^\circ F$, each obtained from Table 6, Appendix A, Hottel, Williams, and Satterfield (2). Q_V at $100^\circ F$ is the heat evolved in cooling the species, and oxygen required for combustion, down to $0^\circ K$, plus the heat of combustion at $0^\circ K$ (E at $0^\circ K$ in Table 6), less the heat absorbed in heating the combustion products from $0^\circ K$ to $311^\circ K (100^\circ F)$.

For the combustion of CO, the combustion equation is:

$$CO + \frac{1}{2} O_2 \longrightarrow CO$$

or one mole of specie CO reacts with one half mole of oxygen to form one mole of CO_2 as combustion products. From Table 6, Appendix A, Hottel, Williams, and Satterfield (2), the following values were obtained:

For CO: $E_{0^\circ K} = 66,769$ For CO_2: $E_{311^\circ K.} - E_{0^\circ K} = 1737$

$E_{311^\circ K.} = 73,757$ For O_2: $E_{311^\circ K.} - E_{0^\circ K} = 1538$

$E_{3600^\circ R} = 78,435$

Then:

$$E_S = E_{3600^\circ R.} - E_{311^\circ K.} = 78435 - 73757 = 4678$$

$$Q_V = \left[E_{311^\circ K} - E_{0^\circ K}\right]_{CO} + \left[E_{311^\circ K} - E_{0^\circ K.}\right]_{O_2} \times \frac{1}{2} + \left[E_{0^\circ K.}\right]_{CO} - \left[E_{311^\circ K.} - E_{0^\circ K}\right]_{CO_2}$$

$$Q_V = (73757 - 66769) + \frac{1538}{2} + 66769 - 1737$$

$$= 72789$$

$$E_{3600^\circ R} = E_S + Q_V$$

$$= 4678 + 72789 = 77467 \text{ calories/g-mole.}$$

The above is the value shown in Table 2.

The value of enthalpy is readily obtained from the relation $H = E + RT$. Thus the enthalpy of CO at $T = 3600°R$ is:

$$H_{3600°R.} = E_{3600°R} + 1.987 \times 2000$$

$$= 77467 + 3974 = 81441 \text{ calories/g-mole}$$

TABLE III

Molar Entropy (at one atmosphere pressure)

Species	3000°	3600°	4500°
CO_2	20.166	22.522	25.791
H_2O	15.910	17.875	20.68
Air-N_2	12.754	14.148	16.072
O_2	13.490	14.956	16.993
CO	12.924	14.336	16.279
H_2	12.061	13.537	15.397
H	8.34	9.26	10.36
OH	12.40	13.74	15.62
NO	13.21	14.65	16.61
O	8.34	9.26	10.38

The units of the above are calories/g-mole °K, or BTU/lb mole °R.

The values shown in the above table (Table III) were obtained from those in Table 6, Appendix A, Hottel, Williams, and Satterfield (2), merely by subtracting the entropy value at the temperature base of the chart (100°F 311°K) from the entropy corresponding to the temperature in question.

TABLE IV

Thermodynamic Properties of Equilibrium Mixture of Combustion Products From Which Charts Were Constructed:

130% AIR

T °R	P psi	E BTU	H BTU	S BTU/	V cu.ft.
3000	800	546.566	752.499	.26154	1.4647
3000	1200	546.546	752.478	.23382	.9764
3000	1500	546.535	752.467	.21402	.7812
3600	800	711.280	959.210	.31680	1.7579
3600	1000	711.174	959.102	.30150	1.4063
3600	1200	711.091	959.021	.28899	1.1719
3600	1400	711.025	958.956	.27842	1.0045
3600	1500	710.997	958.928	.27343	.9375
4500	800	972.820	1281.711	.39186	2.2028
4500	1200	970.082	1278.913	.36448	1.4678
4500	1500	968.667	1277.560	.34939	1.1741

250% AIR

T	P	E	H	S	V
°R	psc	BTU	BTU	BTU/	cu.ft.
3000	800	522.589	728.525	.24276	1.4287
3000	1200	522.576	728.513	.21533	.9524
3000	1500	522.570	728.508	.20005	.7620
3600	800	682.240	930.719	.24695	1.7115
3600	1000	682.166	930.645	.28165	1.3718
3600	1200	682.098	930.577	.26915	1.1431
3600	1400	682.056	930.537	.25859	.9798
3600	1500	682.029	930.509	.25389	.9145
4500	800	927.830	1236.720	.36928	2.1468
4500	1200	925.784	1235.127	.34204	1.4308
4500	1500	925.440	1234.331	.32676	1.1446

The material basis consitent with the above values is one pound of dry air (1/28.95 pound-mole), plus the corresponding fuel.

APPENDIX II

Method of Calculating Composition of Combustion Products In Equilibrium

The large number of molecular species present in the combustion equilibrium mixture makes it necessary to organize the method of calculation to minimize trial-and-error.

There are four kinds of atoms present (C, H, O, N). These are distributed in ten species (CO_2, H_2O, O_2, N_2, CO, H_2, H, OH, NO, O). Available in relating these species are the six chemical equilibrium equations shown in Table I, Appendix I. They are listed again here for convenient reference, with the number of moles of each species being represented by its chemical symbol in parenthesis:

Eq. 1 $K_1 = P_{CO} P_{H_2O}/P_{CO_2} P_{H_2} = (CO)(H_2O)/(CO_2)(H_2)$

Eq 2. $K_2 = P_{NO} P_{H_2}/P_{H_2O} P_{N_2}^{1/2} = (NO)(H_2)/(H_2O)(N_2)^{1/2} \times \sqrt{P/\Sigma}$

Eq. 3 $K_3 = P_{O_2} P_{H_2}^2/P_{H_2O}^2 = (O_2)(H_2)^2/(H_2O)^2 \times \frac{P}{\Sigma}$

Eq. 4 $K_4 = P_O P_{H_2}/P_{H_2O} = (O)(H_2)/(H_2O) \times P/\Sigma$

Eq. 5 $K_5 = P_H/P_{H_2}^{1/2} = (H)/(H_2)^{1/2} \times \sqrt{P/\Sigma}$

Eq. 6 $K_6 = P_{OH} P_{H_2}^{1/2}/P_{H_2O} = (OH)(H_2)^{1/2}/(H_2O) \times \sqrt{P/\Sigma}$

In the above, P is the total pressure in atmospheres, P_i is the partial pressure in atmospheres of each molecular species, and the symbol Σ represents the sum of the moles of all species present.

As shown in Chapter III (4), with a fuel-air ratio of 0.77, or 130% air, there are 1.95 moles of O_2 and 7.332 moles of N_2 present, giving 9.282 moles of air per mole of fuel; with a fuel-air ratio of) .4, or 250% air, there are 3.75 moles of O_2 and 14.1 moles of N_2 present, giving 17.85 moles of air per mole of fuel. If one mole of carbon and of hydrogen in the fuel is chosen as a basis, there are available the following

four equations satisfying the material balance of the four atoms present (C, H, O, N). These equations are, on a mole basis, at equilibrium:

Eq. 7 $(CO_2) + (CO) = 1.000$

Eq. 8 $(H_2O) + (H_2) + \frac{1}{2}[(H) + (OH)] = 1.000$

Eq. 9 $(CO_2) + (O_2) + \frac{1}{2}[(H_2O) + (CO) + (OH) + (NO) + (O)] = 3.75$

Eq. 10 $(N_2) + \frac{1}{2}(NO) = 14.1$

The equations 1 to 10 inclusive give sufficient relations to solve for the composition of the ten molecular species in the combustion products.

Procedure: The first step is to divide the ten species into major components (CO_2, H_2O, O_2, N_2, CO and H_2), and minor components (H, O, NO, and OH) and to consider for the first approximation of composition that only major components are present. Then equations 7 to 10 inclusive become:

Eq 7A $(CO_2) + (CO) = 1.000$

Eq. 8A $(H_2O) + (H_2) = 1.000$

Eq. 9A $(CO_2) + (O_2) + \frac{1}{2}[(H_2O) + (CO)] = 3.75$

Eq. 10A $(N_2) = 14.1$

Eq. 11 $\Sigma = (CO_2) + (H_2O) + (O_2) + (N_2) + (CO_2) + (H_2)$

By judicious use of the above five equations together with equations 1 and 3, a first approximation of the number of moles of the major species present may be obtained. Then, using these results, plus equations 2, 4, 5 and 6, a first approximation of the minor species is made. The values of the minor species so obtained are put onto the original four equations 7, 8, 9, and 10 and these equations in turn solved in terms of the major species. A second approximation is now

carried out, in precisely the same manner as the first approximation, to give corrected values of the major species based upon the presence of minor species. Again values of the minor species are determined with the aid of equations 2, 4, 5 and 6. If the results for all species satisfy equations 7, 8, 9, and 10, the computation is completed; if not, further approximations are carried through until these equations are perfectly satisfied.

To illustrate the method, a sample calculation will be carried out, using representative values of temperature and pressure.

$T = 3000°$ $p = 1200$ psi $P = 81.65$ atmospheres 250% air

From Table I, Appendix I, at $T = 3000°$ R.

$K_1 = 3.406$ $K_4 = 3.981 \times 10^{-10}$

$K_2 = 9165 \times 10^{-8}$ $K_5 = 1.014 \times 10^{-4}$

$K_3 = 1.816 \times 10^{-10}$ $K_6 = 5.053 \times 10^{-6}$

$$\text{Eq. 1.} \quad \frac{(CO)(H_2O)}{(CO_2)(H_2)} = K_1 = 3.406$$

$$\text{Eq 3.} \quad \frac{(O_2)(H_2)^2}{(H_2O)^2} = K_3\left[\frac{\Sigma}{P}\right] = 1.816 \times 10^{-10}\left[\frac{\Sigma}{P}\right]$$

or

$$\frac{(H_2)}{(H_2O)} = 1.347 \times 10^{-5}\left[\sqrt{\frac{\Sigma}{P(O_2)}}\right]$$

Adding equations 7A, 8A, and 10A:

$$\text{Eq. 12} \quad (CO_2) + (CO) + (H_2O) + (H_2) + (N_2) = 16.1$$

$$\text{Eq. 13} \quad \Sigma = 16.1 + (O_2)$$

Multiplying equation 9A by two and subtracting equation 7A:

$$\text{Eq. 14.} \quad (CO_2) + (H_2O) + 2(O_2) = 6.5$$

From equation 10A

$$(N_2) = 14.1$$

1ST APPROXIMATION

		1.	2.
(O_2)		2.25009	2.2500094
$\Sigma = 16.1 + (O_2)$	$\boxed{\text{Eq 13}}$	18.35009	18.3500094
$\sqrt{\frac{\Sigma}{P(O_2)}}$		.316035	.316035
$\frac{(H_2)}{(H_2O)} = 1.347\times10^{-5}\sqrt{\frac{\Sigma}{P(O_2)}}$	$\boxed{\text{Eq. 3}}$	$.42569\times10^{-5}$	$.4257\times10^{-5}$
(H_2)		.0000042569	.000004257
$(H_2O) = 1.000-(H_2)$	$\boxed{\text{Eq 8A}}$	.9999957431	.999995743
$(CO_2) = 6.5-2(O_2)-(H_2O)$	$\boxed{\text{Eq. 14}}$	——	.999985457
$(CO) = 1.000-(CO_2)$	$\boxed{\text{Eq. 7A}}$	——	.00014543
$\frac{(CO)(H_2O)}{(CO_2)(H_2)} = 3.406$	$\boxed{\text{Eq. 1}}$	——	3.410

Eq. 5 $$(H) = (K_5)\cdot(H_2)^{1/2}\cdot\sqrt{\frac{\Sigma}{P}}$$

$$= 1.014\times10^{-4}\times .000004257^{\,1/2}\times\sqrt{\frac{18.3500094}{81.65}}$$

$$= .0000000992$$

Eq. 6 $$(OH) = (K_6)\cdot\frac{(H_2O)}{(H_2)^{1/2}}\sqrt{\frac{\Sigma}{P}}$$

$$= (5.053\times10^{-6})\,\frac{(.999995743)}{(.000004257)^{1/2}}\cdot\sqrt{\frac{18.3500094}{81.65}}$$

$$= .00116094$$

Eq. 2 $$(NO) = K_2 \cdot \frac{(H_2O)}{(H_2)} \cdot (N_2)^{1/2} \cdot \sqrt{\frac{\varepsilon}{P}}$$

$$= (9.165 \times 10^{-8}) \cdot \frac{.999995743}{.000004257} \cdot 14.1^{1/2} \sqrt{\frac{18.3500094}{81.65}}$$

$$= .0383043$$

Eq. 4 $$(O) = K_4 \cdot \frac{(H_2O)}{(H_2)} \cdot \frac{\varepsilon}{P}$$

$$= (3.981 \times 10^{-10}) \cdot \frac{.999995743}{.000004257} \cdot \frac{18.3500094}{81.65}$$

$$= .0000\,21015$$

Substituting these values for the minor species in equations 7, 8, 9 and 10:

Eq. 7 $$(CO_2) + (CO) = 1.000$$

Eq. 8 $$(H_2O) + (H_2) = 1.000 - \tfrac{1}{2}\left[(H) + (OH)\right]$$

$$= .9994\,1948$$

Eq. 9 $$(CO_2) + (O_2) + \frac{1}{2}\left[(H_2O) + (CO)\right] = 3.750 - \frac{1}{2}\left[(OH) + (NO) + (O)\right]$$

$$= 3.730247$$

Eq. 10 $$(N_2) = 14.1 - \tfrac{1}{2}(NO)$$

$$= 14.080848$$

Now, following the same procedure as before:

Adding Eq. 7, 8, and 10:

Eq. 12A $(CO_2)+(CO)+(H_2O)+(H_2)+(N_2)=16.0802675$

Eq. 13A $\Sigma = 16.0802675+(O_2)$

Multiplying Eq. 9 by two and subtracting Eq. 7:

Eq. 14A $(CO_2)+(H_2O)+2(O_2)=6.460494$

2ND APPROXIMATION

	1.	2.
(O_2)	2.23055	2.2305437
$\Sigma = 16.080257+(O_2)$	18.310807	18.3108007
$\sqrt{\frac{\Sigma}{P(O_2)}}$	.317071	.317071
$(H_2)/(H_2O) = 1.347\times10^{-5}\sqrt{\frac{\Sigma}{P(O_2)}}$	$.42709\times10^{-5}$	$.42709\times10^{-5}$
(H_2)	.00000427	.00000427
$(H_2O)=0.99941947-(H_2)$	.99941520	.9994152
$(CO_2)=6.460492-2(O_2)-(H_2O)$	——	99998545
$(CO) = 1.000 - CO_2$	——	.00001455
$\frac{(CO)(H_2O)}{(CO_2)(H_2)} = 3.406$		3.405

Again determining the minor species from Eqs. 5, 6, 2 and 4:

$(H) = .0000000992$

$(OH) = .00115729$

$(NO) = .038121$

$(O) = .000020895$

The values of these species have not changed from those obtained in the first approximation, to any extent, and hence all values satisfy equations 7,8, 9 and 10; if they had not, a third approximation would have been required, performed in the same manner as the above.

Final Results:

$(CO_2) = .99998545$

$(H_2O) = .9994152$

$(O_2) = 2.2305437$

$(N_2) = 14.08094$

$(CO) = .00001455$

$(H_2) = .00000427$

$(H) = .0000000992$

$(OH) = .00115729$

$(NO) = .038121$

$(O) = .00020895$

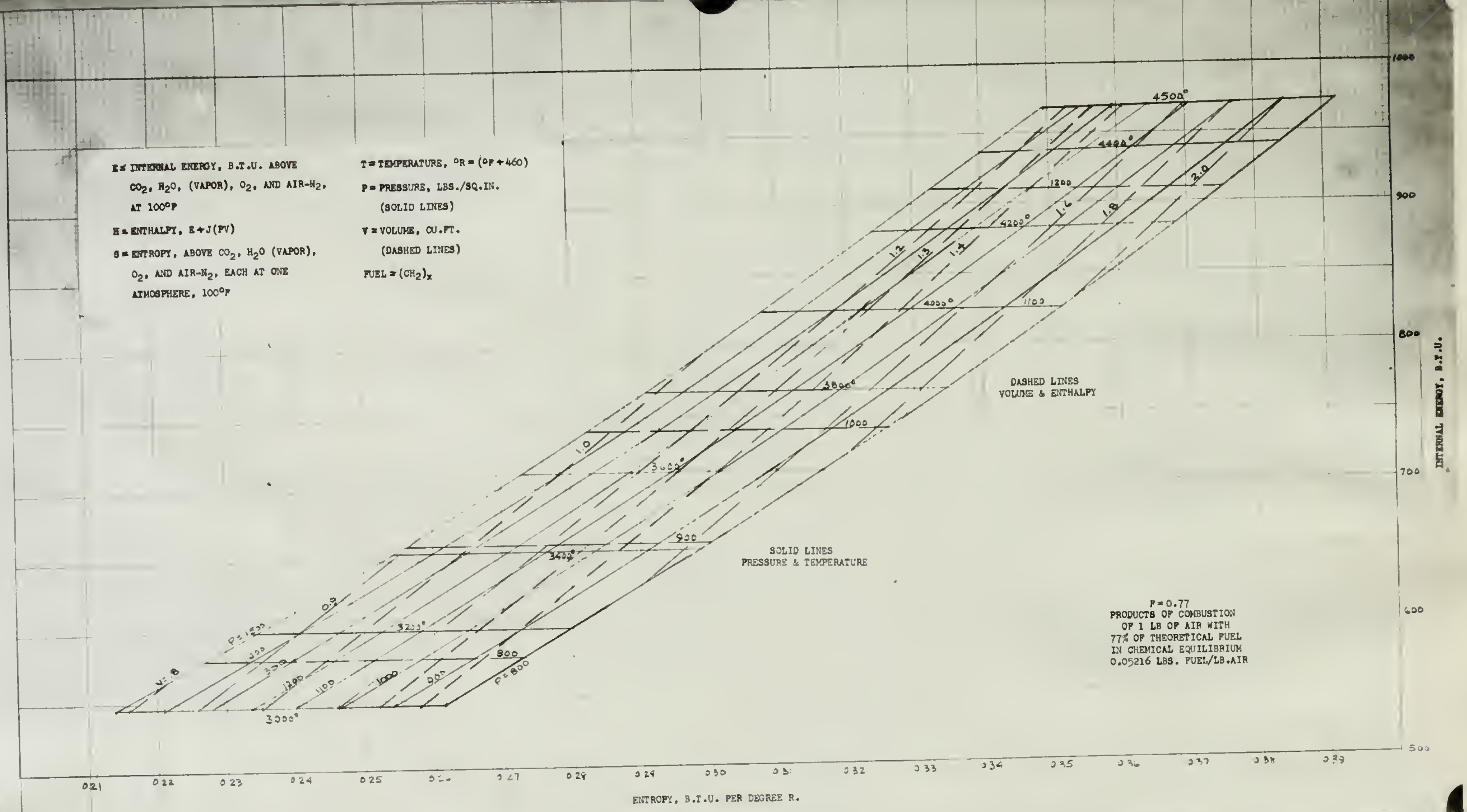
E = INTERNAL ENERGY, B.T.U. ABOVE CO_2, H_2O, (VAPOR), O_2, AND AIR-H_2, AT 100°F
H = ENTHALPY, E + J(PV)
S = ENTROPY, ABOVE CO_2, H_2O (VAPOR), O_2, AND AIR-N_2, EACH AT ONE ATMOSPHERE, 100°F
T = TEMPERATURE, °R = (°F + 460)
P = PRESSURE, LBS./SQ.IN. (SOLID LINES)
V = VOLUME, CU.FT. (DASHED LINES)
FUEL = $(CH_2)_x$
4500°
4400°
4200°
4000°
3800°
3600°
3400°
3200°
3000°
2.0
1.8
1.6
1.4
1.3
1.2
1.0
0.9
V = .8
P = 1500
1300
1200
1100
1000
900
P = 800
DASHED LINES
VOLUME & ENTHALPY
SOLID LINES
PRESSURE & TEMPERATURE
F = 0.77
PRODUCTS OF COMBUSTION
OF 1 LB OF AIR WITH
77% OF THEORETICAL FUEL
IN CHEMICAL EQUILIBRIUM
0.05216 LBS. FUEL/LB.AIR
INTERNAL ENERGY, B.T.U.
1000
900
800
700
600
500
ENTROPY, B.T.U. PER DEGREE R.
0.21
0.22
0.23
0.24
0.25
0.26
0.27
0.28
0.29
0.30
0.31
0.32
0.33
0.34
0.35
0.36
0.37
0.38
0.39

Fig I

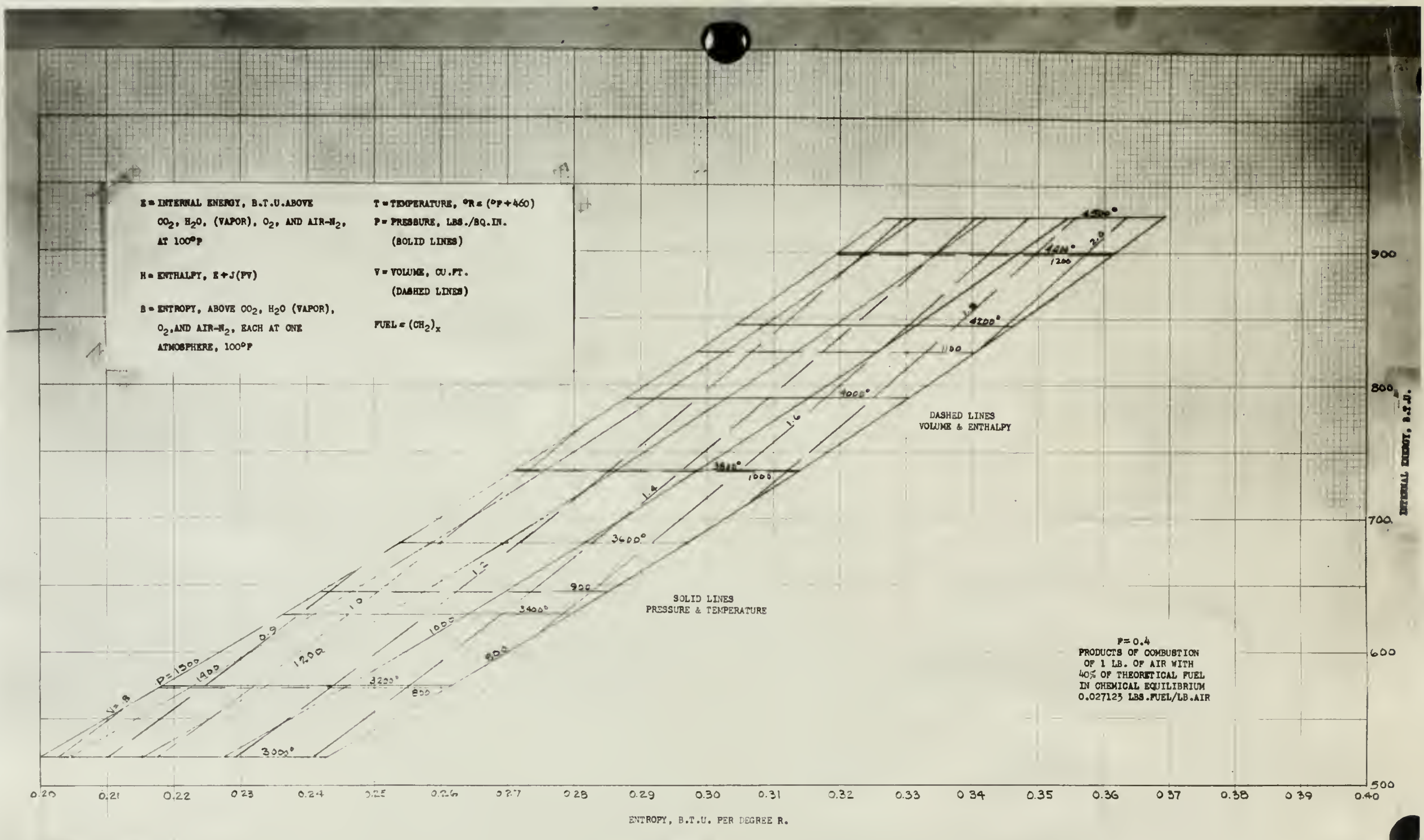
E = INTERNAL ENERGY, B.T.U. ABOVE CO2, H2O, (VAPOR), O2, AND AIR-N2, AT 100°F
H = ENTHALPY, E + J(PV)
S = ENTROPY, ABOVE CO2, H2O (VAPOR), O2, AND AIR-N2, EACH AT ONE ATMOSPHERE, 100°F
T = TEMPERATURE, °R = (°F + 460)
P = PRESSURE, LBS./SQ.IN. (SOLID LINES)
V = VOLUME, CU.FT. (DASHED LINES)
FUEL = (CH2)x
DASHED LINES
VOLUME & ENTHALPY
SOLID LINES
PRESSURE & TEMPERATURE
F = 0.4
PRODUCTS OF COMBUSTION
OF 1 LB. OF AIR WITH
40% OF THEORETICAL FUEL
IN CHEMICAL EQUILIBRIUM
0.027123 LBS.FUEL/LB.AIR
4500°
4400°
4200°
4000°
3800°
3600°
3400°
3200°
3000°
2.0
1.8
1.6
1.4
1.2
1.0
0.9
V = 8
P = 1500
1400
1200
1100
1000
900
800
ENTROPY, B.T.U. PER DEGREE R.
INTERNAL ENERGY, B.T.U.
0.20
0.21
0.22
0.23
0.24
0.25
0.26
0.27
0.28
0.29
0.30
0.31
0.32
0.33
0.34
0.35
0.36
0.37
0.38
0.39
0.40
500
600
700
800
900

Fig Ia

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Thermodynamic chart for the combustion process in diesel cycles.

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